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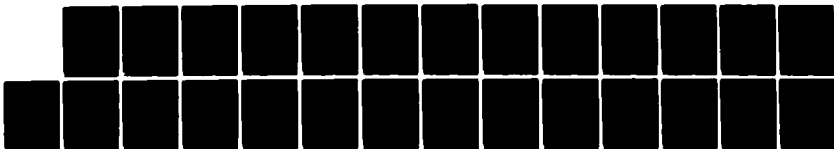
CLARIFICATION OF ENVIRONMENTAL EFFECTS IN STRESS
CORROSION CRACKING(U) AMERICAN UNIV WASHINGTON DC
R T FOLEY JAN 84 N00014-75-C-0799

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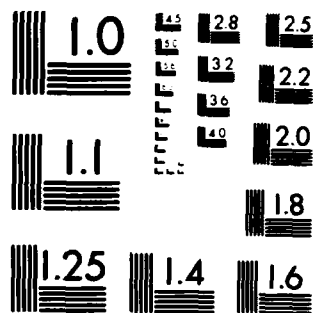


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this project was to clarify the role of the environ- ment in the stress corrosion cracking and the localized corrosion of aluminum alloys. Specifically, the project addressed the manner in which different chemical species, such as various anions, are involved in the corrosion process. continued on reverse		

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This objective was accomplished by the application of chemical and electrochemical techniques in the investigation of the corrosion process and then testing the interpretation of these results with stress corrosion cracking tests (DCB specimens).

The corrosion process was studied with scrape potential measurements, quantitative pitting kinetic studies, UV and IR examination of aluminum salt solutions, analytical studies to determine actual concentrations and pH's of the solution in pits and stress corrosion cracks, and scanning electron microscope examination of stress cracks. Stress corrosion cracking tests were conducted with double cantilever beam (DCB) specimens and the data were analyzed statistically to establish the reliability of the test.

Out of this study, a four step mechanism evolved to explain localized corrosion. The four steps, adsorption, chemical reaction, film thinning, and direct attack on the metal were studied independently.

The unifying concept, most useful in explaining localized corrosion, of which pitting and stress corrosion cracking are examples, is the complex ion theory of corrosion. This theory states that the critical element in the corrosion process is the nature of the first formed chemical species that appear upon dissolution of the metal. If transitory, soluble, metal-anion complex ions are formed, the reaction will proceed rapidly. If stable, covalent, compounds are formed, the metal will tend to passivate.

By the application of this concept it is possible to interpret all of the experimental data obtained on this project and, indeed, all of the experimental data reported in the literature.

Indices of the technical reports and the publications issued as a result of the work on the project are given.

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"Clarification of Environmental Effects on
Stress Corrosion Cracking"

Contract N00014-75-C-0799, NR 036-106

FINAL REPORT

One of the critical problems in the materials field is the stress corrosion cracking of metals. This problem cuts across all areas of technology in this country, both civilian and military, and is of critical importance particularly in those areas that require high strength alloys to operate in high reliability service, such as in aircraft and in nuclear power reactors. Stress corrosion cracking is a conjoint phenomenon involving mechanical features and environmental features. Thus, the solution of the problem, or even its investigation, requires the elucidation of metallurgical factors and environmental factors. It is in the latter area that our program has mainly contributed, specifically, by the introduction and application of a new scientific concept to the explanation of the effect of environment in the stress corrosion cracking problem.

The concept, introduced and evaluated on our program, states that the environment enters into the corrosion process principally through the formation of transitory metal-anion species, usually complex ions, the nature of which directs the ensuing reaction to one of rapid dissolution, on one hand, or to passivation on the other. The development and the demonstration of the validity of this concept was achieved with experimental data drawn from a number of different techniques, such as immersion tests, scrape potential determinations, pitting kinetics, inhibition studies, "local chemistry" analyses, and double-cantilever specimen stress corrosion cracking tests. These findings are summarized in the following paragraphs.

SUMMARY OF WORK

The findings and observations from the various experimental techniques have been synthesized in the form of a multi-step mechanism for localized corrosion, including pitting and stress corrosion cracking. The four steps involved in the process are:

- I. The adsorption of the reactive anion on the oxide-covered aluminum.
- II. The chemical reaction of the adsorbed anion with the aluminum ion in the aluminum oxide lattice or on the precipitated aluminum hydroxide.
- III. The thinning of the oxide film by dissolution.
- IV. The direct attack of the exposed metal by the anion, perhaps, assisted by an anodic potential.

This mechanism evolved from, and is supported by, the experimental findings reported in detail in the papers listed in INDEX OF PUBLICATIONS below.

I. THE ADSORPTION STEP

The adsorption of anions on the oxide-covered aluminum surface which would promote pitting corrosion has been viewed traditionally as a competitive process. That is, chloride or another aggressive ion is adsorbed competitively with hydroxyl ions or water molecules which would, if adsorbed, tend to promote passivity.

There is substantial experimental evidence for the adsorption of anions and particularly for the adsorption of chloride as a preliminary step to pitting. It was not necessary for us to do any experimental work to confirm the validity of this proposed step.

II. THE CHEMICAL REACTION STEP

The Engell-Stolica method has been very useful in establishing the nature of the species involved at this stage. In the Engell-Stolica method the aluminum electrode is potentiostated in the passive range, a known concentration of an aggressive anion is injected into the solution, and the "induction time" for pitting is measured. This induction time is the time required for a sharp rise in the anodic current to occur. A relationship between the induction time and concentration of the aggressive anion allows an estimation of n , the number of anions associated with a single surface site during the primary pitting process.

Determinations of the stoichiometric number for the pitting of aluminum and two aluminum alloys in chloride and bromide solution are given in Table I. These results suggest that a low pH, about one, species such as AlBr_4^- are formed, at neutral pH's, AlBr^{++} , and at intermediate pH's, complexes with $n = 2$ to 3. The energies of activation for the pitting reactions in bromide and chloride solution are in the range indicative of a chemical reaction. They are higher in the acid solution, pH = 3, than at pH = 5.8, in agreement with the order of reaction (Table II.) The "induction time", τ , in the Engell-Stolica method is interpreted in a statistical sense. It measures an average rate of reaction over the whole surface to produce a measurable rise in current.

To summarize the results of experiments dealing with the chemical reaction - results obtained mainly in our own laboratory, but supported by results reported in the literature, it can be said that there is substantial evidence for the formation of well-characterized aluminum-anion reaction products. The first of these are aluminum complex ions such as AlCl^{++} ,

Table I Stoichiometric number, n , for pitting of aluminum alloys
by Cl^- and Br^-

Alloy	Aggressive anion	pH	Order of reaction, n
Al 1199	Cl^-	0.00	$n = 4$
Al 7075	Cl^-	0.3	$n = 4-8$
Al 7075	Br^-	0.3	$n = 4$
Al 1199	Cl^-	3.56	$n = 1.5$
Al 1199	Br^-	3.56	$n = 2.5$
Al 7075	Br^-	5.8	$n = 2$
Al (99.995%)	Cl^-	6.0	$n = 2$
Al 7075	Cl^-	5.8	$n = 2$
Al 1199	Cl^-	5.9-6.1	$n = \sim 1$
Al (99.53%)	Cl^-	neutral	$n = \sim 1$

Table II Activation energies for pitting initiation reaction of
aluminum alloy Type 7075 with halides

Anion	E_a (kcal mole ⁻¹)	
	pH 0.3	pH 5.8
F-	---	4.6
Cl-	18	12
Br-	26	10
I-	6.6	---

AlCl_4^- , $\text{Al}(\text{OH})\text{Cl}_2$, and $\text{Al}(\text{OH})_2\text{Cl}$ which may be transitory. The second are stable, covalent, compounds like those formed with SO_4 , such as the basic aluminum sulfate $[\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$.

On this basis it is then possible to represent the chemical reaction between aluminum and chloride ion by a potential energy surface as shown in figure 1. Starting on the left, the reaction may be followed with the high energy atomic aluminum reacting with chloride ion to form transitory complexes, soluble hydroxy chloride species, and finally stable, low energy compounds such as Al_2O_3 and $\text{Al}(\text{OH})_3$.

III. THE THINNING OF THE OXIDE

The protective oxide on aluminum has been traditionally regarded as inert. That is, although the film may include cracks or fissures, it did not dissolve in aqueous solutions. Such is not an accurate view of the oxide film. Considering alumina, ($\alpha\text{-Al}_2\text{O}_3$), which would be expected to be more stable than the oxide film on aluminum metal, the solubility in various concentrations of NaCl is reported in Table III. With regard to this analysis it should be mentioned that aluminum exists in solution as (a) monomeric species, as Al^{+++} , $\text{Al}(\text{OH})^{++}$, $\text{Al}(\text{OH})_2^+$, and $\text{Al}(\text{OH})_4^-$; (b) polynuclear species containing 20-100 Al atoms; and (c) large, solid $\text{Al}(\text{OH})_3$ particles; all depending, of course, on the pH of the solution. The analysis given in Table III was done spectrophotometrically with Eriochrome Cyanine R reagent and only measured the monomeric species. It did not measure the concentration of polymers with a basic unit structure of $\text{Al}(\text{OH})_2\text{Cl}$ which would be expected to form in light of the above discussion. But, these experiments did demonstrate that alumina is indeed soluble in aqueous solutions.

These results are in agreement with other investigations reported in the literature and cited in the complete papers, and all of these studies

Fig. 1- Al-Cl Potential Energy Surface

Table III Amount of aluminum ions dissolved in 100 ml of different NaCl concentration solutions

Concentration of NaCl	Aluminum powder (10g)	Alumina (10g)
1.00N	41 \pm 2 μ g	231 \pm 14 μ g
0.75N	54 \pm 3 μ g	258 \pm 15 μ g
0.50N	65 \pm 4 μ g	322 \pm 19 μ g
0.35N	54 \pm 3 μ g	358 \pm 21 μ g
0.25N	54 \pm 3 μ g	433 \pm 28 μ g
0.10 N	67 \pm 4 μ g	476 \pm 28 μ g

offer independent evidence for the proposition that even in the absence of other effects, mechanical, etc. the oxide film on aluminum would be expected to be thinned upon exposure to aqueous solution.

IV. DIRECT ATTACK OF EXPOSED METAL

Once the film is sufficiently thinned, the high degree of reactivity of metallic aluminum insures rapid attack and pit propagation. Because the film is thinned locally, the attack on the metal will also be concentrated in the geometrical sense. It should be emphasized that this step, the direct attack of the exposed metal, differs in a basic manner from the pit initiation reaction. The initiation reaction is concerned with the interaction, chemically or physically, of the oxide film with the solution (the environment). The growth of the pit, the propagation of the pit, involves the interaction of aluminum metal directly with an environment that is changing as the reaction proceeds. Recognizing this different behavior, then the futility of disclosing a single phenomenon to correlate the entire four-step pitting process becomes evident.

With regard to the propagation of pits resulting from the direct attack of the metal by the environment we have made microscopic observations of the pits formed on AA 7075 in halide solution, excluding fluoride solution, and found that the pits were predominantly hemispherical. The rate of propagation expressed as current as a function of time took the form

$$i - i_p = a(t - t_i)^b \quad (8)$$

where i = the dissolution current; i_p = the passive current; t = time; t_i = induction time; a = a constant dependent on the halide; and b = a constant dependent on the geometry of the pit.

The current-time relationship is derived from a plot of $\log (i - i_p)$ vs $\log (t - t_i)$, the slope of which gives "b". With this treatment, it was found

that the pit propagation rate was anion dependent and for three anions could be represented by cubic equations as

$$\begin{aligned}\text{for } 3 \times 10^{-2} \text{NI}^- \quad (i-i_p) &= 0.073(t-t_i)^3 \\ \text{for } 4 \times 10^{-3} \text{NCl}^- \quad (i-i_p) &= 0.0051(t-t_i)^3 \\ \text{for } 8 \times 10^{-3} \text{NBr}^- \quad (i-i_p) &= 0.00195(t-t_i)^3\end{aligned}$$

It is important to recognize that the behavior of aluminum alloys described here probably represents a special case insofar as the curves experimentally yield a $b=3$ or exhibit cubic behavior.

The morphology of the pit is affected by the potential as well as the specific anion involved in the pitting reaction. We have observed, along with others, that the applied potential does influence the morphology of the pits that are formed on AA 1199 in chloride solution. At low potential $E_{\text{appl.}}$, (620mV), the pits formed were hemispherical, while at high $E_{\text{appl.}}$, (1860 mV), the pit mouth was covered by a porous layer film with a small central orifice. It was also observed that gas bubbles out through this small orifice during the pitting process.

It has long been recognized that the composition of the solution within the corrosion pit differs substantially from that in bulk solution. This also holds for the solution in a crevice and the advancing crack of a stress corrosion cracking specimen. Without knowledge of the pH of this solution and the chemical composition, including Al^{+++} ion concentration and anion concentration, it would not be possible to characterize the composition of the "occluded cell" sufficiently to formulate a reasonable mechanism for the pitting process. For this reason a considerable amount of effort has been expended to analyze the solution in a stress-corrosion crack, in pits and crevices, both artificial and naturally occurring. Generally speaking, these analyses are quite close to each other.

Unfortunately, most of the experimental work on the occluded cell has been done in chloride solution, and the results, e.g. an observed pH of 3.2, have been extrapolated to all electrolytic solutions. Recently the analysis of the solutions obtained with the freeze-thaw technique of Brown from stress corrosion cracks in AA 7076 cracked in 1N NaCl, Na₂SO₄, NaNO₃ and NaClO₄ have been completed. A summary of the pH's in the crack and the pre-crack zone (which resembles a crevice) are given in Table IV.

The corresponding Al⁺⁺⁺ ion analyses are given in Table V.

These results demonstrate that the behavior in chloride, and to some degree sulfate, differs appreciably from that in nitrate, perchlorate, and H₂O. The results in perchlorate are of special interest because perchlorate ion does not form metal-anion complexes. These results were unexpected. Following, what had been reported in the literature it had been assumed that at the anode, the tip of the crack, Al⁺⁺⁺ would go into solution and a concentrated solution of the aluminum salt of the respective anion would be formed. The corrosion rates of AA 1199 and AA 7075 had been determined in 0.1N, 0.2N, and 0.5N solutions of Al(NO₃)₃, AlBr₃, AlCl₃, Al₂(SO₄)₃, AlClO₄, and AlI₃. The corrosion rates varied with the salt but for all of these solutions the rates were very high. All of these salts are the neutralization products of the respective strong acid and the weak base, Al(OH)⁺⁺. These salts upon hydrolysis gave pH's for the 0.5M solution of 1.10 to 3.49 with most about 2.5. Therefore, it was expected that the analyses of the solution in the stress corrosion crack for the four electrolytes would be approximately the same. These latest findings lead to the conclusion that, insofar as the solution in the advancing crack of a stress corrosion cracking specimen is concerned, the pH and the aluminum concentration are anion dependent. There was not evidence for very concentrated solutions of the aluminum

Table IV Analysis of Stress Corrosion Crack Solutions - pH measurements.

Electrolyte	pH			
	Crack tip	Corrosion product region	Pre-crack region	Bulk solution
1N NaCl	3.0-3.2	4.2-4.5	4.6-5.0	7.0-7.2
1N NaClO ₄	6.1-6.3	6.6-6.9	6.9-7.2	7.0-7.2
1N NaNO ₃	5.9-6.1	6.6-6.9	7.0-7.2	7.0-7.2
1N Na ₂ SO ₄	6.1-6.3	2.8-3.0	4.0-4.3	7.0-7.2
H ₂ O	6.6-6.9	6.9-7.2	6.9-7.2	6.9-7.2

Table V Analysis of Stress Corrosion Crack Solutions - Aluminum
Ion Concentration and Potential

Electrolyte	Concentration of Al ⁺⁺⁺ (molar)		Potential of Bulk Solution (vs SHE)	Plateau Crack Rate (10 ⁶ cm sec ⁻¹)
	Corrosion crack region	Precracked region		
1N NaCl	0.025(10)*	0.36(5)	-0.588 V	1.43
1N NaClO ₄	0.008(9)	0.39(8)	-0.524 V	0.81
1N NaNO ₃	0.005(5)	0.18(5)	-0.111 V	0.48
1N Na ₂ SO ₄	0.005(5)	0.36(6)	-0.443 V	0.29
H ₂ O	-	-	-	0.61

*number of measurements that were averaged to get the reading reported

salt and certainly no evidence for precipitated salt films as has been reported in the literature.

One complicating factor that has been observed in the examination of stress corrosion cracks and presumably will be observed in pits and crevices is the alteration of the chemical species as the reaction ensues. It is known that nitrate is reduced by elemental aluminum in alkaline solution, which alkaline solution can be produced in the pit at the cathodic site, $8\text{Al} + 3\text{NO}_3^- + 5\text{OH}^- + 18\text{H}_2\text{O} \rightarrow 8\text{Al}(\text{OH})_4^- + 3\text{NH}_3$. When a solution of NaNO_3 was brought in contact with aluminum powder, the formation of ammonia could be recognized after 16 hours. Upon shaking the suspension vigorously, the formation of NH_3 was quickly accelerated and within a few minutes, the heat generated by the reaction brought the whole solution to complete ebullition. Since no such formation of NH_3 was observed in the case of alumina, it was concluded that NH_3 was the product of the chemical reaction between NO_3^- and the underlying aluminum metal.

STRESS CORROSION CRACKING TESTS

The "reduction to practice" of the theoretical concepts developed on this project must be done through practical stress corrosion tests. In our study double cantilever beam (DCB) specimen were used to measure the rate of crack growth.

Surprisingly enough, there was virtually no information in the literature regarding the accuracy or precision of the DCB test, or indeed, of stress corrosion tests in general. The measurement of the rate of stress corrosion cracking of AA 7075-T651 was conducted in 1N NaClO_4 , 1N NaCl , 1N Na_2SO_4 , and 1N H_2O_2 solution and that data were treated statistically to arrive at a measure of reliability of the test. The complete analysis is given in the attached reprint of a paper which appeared in the October 1983 issue of CORROSION but some general observations may be made. The crack

growth rate in NaClO_4 solution, noting that perchlorate is a non-complexing anion, was $0.81 \times 10^{-6} \text{ cm sec}^{-1}$ as compared with 1N HCl with a rate of $1.43 \times 10^{-6} \text{ cm sec}^{-1}$. Solutions of NaNO_3 and Na_2SO_4 gave rates of $0.48 \times 10^{-6} \text{ cm sec}^{-1}$ and $0.29 \times 10^{-6} \text{ cm sec}^{-1}$ respectively. The statistical analysis of the data established a reliability of 5 - 10% for these measurements.

Stress corrosion cracking tests were conducted in a large number of electrolytes and these results are summarized in Table VI. In general, the substances which activate the aluminum surface, as by forming soluble complexes with aluminum, caused rapid cracking. There were some exceptions, for example, benzoate, which inhibited corrosion but promoted stress corrosion cracking. The activity of water in aqueous solutions of various salts did not correlate directly with the cracking rate as had been claimed by other investigators. Specific ion effects are dominant.

Table VI Solutions used in DCB Stress Corrosion Tests

Sodium sulfate- Na_2SO_4	1N(0.5M), 0.01N (0.005M)
Potassium sulfate- K_2SO_4	1N (0.5M)
Sodium chloride- NaCl	0.01N (0.01M), 0.6N (0.6M), 1N (1M), 3N (3M), 6.5N (6.5M)
Sodium perchlorate- NaClO_4	1N (1M)
Sodium chromate- Na_2CrO_4	1N (0.5M)
Sodium dichromate- $\text{Na}_2\text{Cr}_2\text{O}_7$	1N (0.5M)
Sodium nitrate- NaNO_3	1N (1M)
Sodium nitrite- NaNO_2	1N (1M)
Sodium ortho-phosphate- Na_3PO_4	1N (0.33M)
Sodium carbonate- Na_2CO_3	1N (0.5M)
Sodium acetate- NaCH_3COO	1N (1M)
Sodium tartrate- $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$	1N (0.5M)
Sodium oxalate- $\text{Na}_2\text{C}_2\text{O}_4$	1N (0.5M)
Sodium benzoate- $\text{NaC}_7\text{H}_5\text{O}_2$	1N (1M)
Ammonium hydroxide	1N
Dimethyl sulfoxide	

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Stress Corrosion Cracking of AA 7075-T651 in Various Electrolytes—Statistical Treatment of Data Obtained Using DCB Precracked Specimens*

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Abstract

Double cantilever beam specimens were employed to measure the rate of stress corrosion crack growth of AA 7075-T651 in 1 N NaClO₄, 1 N NaCl, 1 N Na₂SO₄, and 1 N NaNO₃ solutions. Perchlorate is a noncomplexing anion, so the tests conducted in NaClO₄ solution should not be affected by specific anion effects. The data were treated statistically to arrive at a measure of the reliability of the test using DCB specimens. The crack growth rate in 1 N NaClO₄ solution was 0.81×10^{-6} cm sec⁻¹, as compared with 1 N NaCl solution, 1.43×10^{-6} cm sec⁻¹; 1 N NaNO₃, 0.48×10^{-6} cm sec⁻¹; and Na₂SO₄, 0.29×10^{-6} cm sec⁻¹. These tests are generally reproducible to about 5 to 10%. The pH of the solution in the advancing crack in NaClO₄ solution was 6.2 to 6.9, as compared with 3.2 in NaCl solution. The Al⁺⁺⁺ concentration was low, in the range of 0.005 to 0.001 M. To study metallurgical effects in the stress corrosion cracking of high strength aluminum alloys, it would be advisable to use perchlorate instead of chloride solutions to avoid specific anion effects.

Introduction

The overall objective of this investigation is to clarify the effect of the environment on the stress corrosion cracking of high strength aluminum alloys. Specifically, the intention is to develop in a quantitative way, the relationship between crack propagation rate and anion concentration. In this study, double cantilever beam (DCB) specimens are used to measure the rate of crack growth.

In evaluating the relative effect of anions, for example, to establish that the rate of crack growth in chloride is some multiple of that in sulfate, the determination of the accuracy and precision of a single test becomes of great significance. However, there is virtually no information in the literature regarding the accuracy or precision of the DCB test, or indeed, of stress corrosion tests in general.

The employment of DCB precracked specimens has been described by Hyatt.¹ The stress analysis and theory have been discussed in detail by Smith and Piper,² and the employment of the test in the investigation of the stress cracking of high strength aluminum alloys has been reported by Hyatt and Speidel.³ A previous communication⁴ from this laboratory has studied the anion dependence of the stress corrosion cracking of AA 7075-T651. However, in none of these reports is there a clear statement of the accuracy or precision of the test.

With regard to accuracy, this assumes the existence of some true value. In any experimental test there are determinant and indeterminant or random errors. In all of the develop-

ment of standard stress corrosion tests, the effort has been to eliminate the determinant errors by selection of specimen geometry, surface finish, etc. If this could be done completely, then it would be possible to establish a true value for crack initiation or crack growth. However, the feasibility of doing this is low. For example, the stress corrosion cracking behaviors of different plates of the same alloy (essentially the same chemical analysis and metallurgical parameters) are considerably different.⁴ In a given plate, there are structural differences between the center of the plate and the edge of the plate with accompanying different stress cracking properties. The fact is that in virtually all real cases two specimens assumed to be identical are actually not identical and this precludes the establishment of a true value.

With respect to precision, this problem has not been addressed directly. Experimental data reporting time-to-failure of stress corrosion specimens have been treated statistically by the application of the Weibull distribution.⁵ The analysis of real data requires a very high number of samples and the distribution of times-to-failure is usually quite wide. Such time-to-failure tests might be useful in evaluating different lots of a given alloy but have limited usefulness in developing mechanistic relationships between factors involved in stress corrosion.

The testing of smooth specimens which are usually used in time-to-failure tests involve not only the initiation of cracking, but also the propagation of cracking. In the use of precracked specimens, the initiation time uncertainty is removed and only propagation is considered.

The problem of environmental influences in stress corrosion cracking has not been broadly attacked. Most testing has been done in NaCl solution with a major variant being the man-

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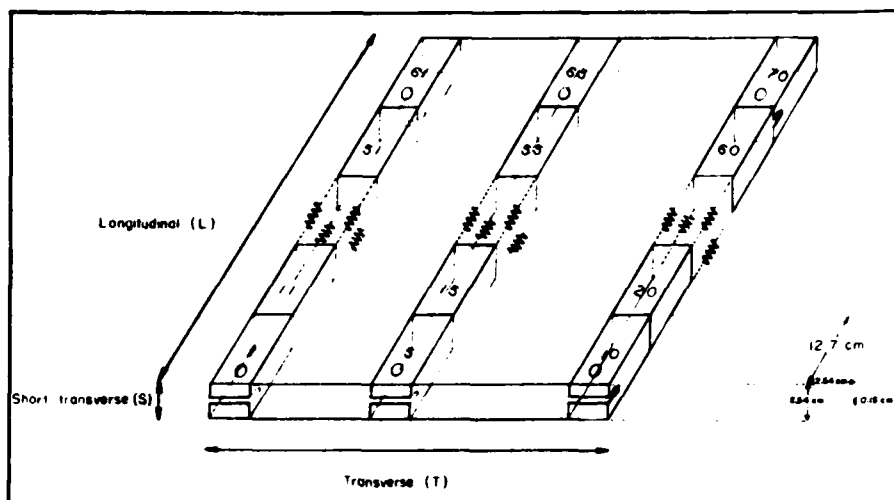


FIGURE 1 — Location of DCB specimens in plate of AA 7075-T651.

ner in which the chloride was introduced, e.g., directly, by alternate immersion, by sea coast atmosphere, or others. A large series of tests was conducted in potassium iodide solution⁶ which is known to react chemically with aluminum. The common feature in these tests is that the electrolyte employed introduces specific anion effects because of the tendency of the anions to complex with aluminum. It then becomes of interest to investigate the stress cracking behavior in a non-complexing anion solution, such as perchlorate, and to compare this behavior with that in solutions with specific interactions. Sodium perchlorate, insofar as it is known, does not complex with aluminum, and, for this reason, should be considered to be an indifferent electrolyte in the sense that it provides a solution with high electrical conductivity but not chemical reactivity.

The purpose of this paper is to report on the stress cracking of AA 7075-T651 in sodium perchlorate solution with appropriate attention being given to the precision of the DCB pre-cracked test results

Experimental

The double cantilever beam (DCB) specimen first used to study stress corrosion cracking by Dahlberg⁷ was employed. The specimens were machined from the plate (plate E in the AU inventory) in such a way that the stress corrosion crack would be located at midplane parallel to the rolling plane and growing in the rolling direction (SL orientation). The specimens were $2.54 \times 2.54 \times 12.7$ cm. To eliminate effects that might be produced by the location of the specimen within the plate, the specimens were systematically taken, as indicated in Figure 1. For example, the nine specimens used for the first experiments with sodium perchlorate solution were numbers 1, 5, 10, 31, 35, 40, 61, 65, and 70. Specimens 10, 40, and 70 were cut from the edge of the plate.

The blanks were slotted with a sharp, thin milling cutter and were provided with opposing bolts to give the same configuration as the double bolt loaded specimens currently being used in the "round robin" exercise under the auspices of ASTM Sub-Committee G01.08. Notch length was 2.2 cm measured from the point of loading (bolt centerline). The specimens were washed in detergent, rinsed in tap water, and held for 5 hours in refluxing acetone. The specimens were pre-cracked by mechanical overload ("pop-in") effected by torquing 2 bolts. One of the bolts was mechanically rounded so that an equal stress could be obtained on both sides of a specimen. The deflection, δ , at the loading line was

monitored with a micrometer. A scale graduated in mm was cemented on each side of the specimen parallel to and near the expected trace of the stress corrosion crack. The scale was then coated with an inert Label Glaze. Upon exposure in the test solution, crack length was observed by using a low power lens and recorded as a function of immersion time. The solutions were prepared with conductivity water (deionized, double distilled in quartz) and evaporation losses were replenished by addition of water when the experiments were conducted over a period of days. The experiments were all conducted at room temperature 24 ± 2 C. Specimens were left undisturbed in solution. However, the corrosion products, as well as the gas bubbles formed at the crack, had to be wiped off prior to measurement.

In a typical experiment, the specimen was removed from the solution after the crack growth had progressed a certain length, frozen in a mixture of dry ice and acetone (-60 C), and then broken apart by mechanical overloading. The specimen was kept in a desiccator while thawing to prevent the adsorption of humidity at room temperature. The pH and aluminum ion concentration were measured immediately after thawing. The pH was determined by pressing a strip of Pehanon pH indicator paper obtained from the Macherey-Nagel Company against the crack. The precision of the pH measurement was ± 0.2 pH units. The concentration of aluminum ion present in the crack was semiquantitatively estimated by comparing the color developed on an indicator paper with a series of colors produced by known concentrations of aluminum perchlorate solutions. The indicator paper was prepared by soaking filter paper in quinalizarin (1, 2, 5, 8-tetrahydroxy anthraquinone) solution,¹⁸ prepared by dissolving 10 mg of quinalizarin in 2 ml of pyridine and diluting with 20 ml acetone. In a typical measurement, the indicator paper was pressed against the specimen at the crack tip region. It was then held for a short time over a bottle containing concentrated ammonia and then over glacial acetic acid until the first formed blue color (ammonium salt of quinalizarin) disappeared and the unmoistened paper regains its brown color. The red violet or faint red fleck color remaining showed the presence of aluminum. This color was then compared to the standard colors produced by solutions of known aluminum concentrations.

The detectable limit of aluminum concentration of this test is 0.5 ppm, and for semiquantitative identification, 5×10^{-9} g. This test is especially reliable for the detection of aluminum in the presence of magnesium. The magnesium content of AA 7075 is about 2.5%.

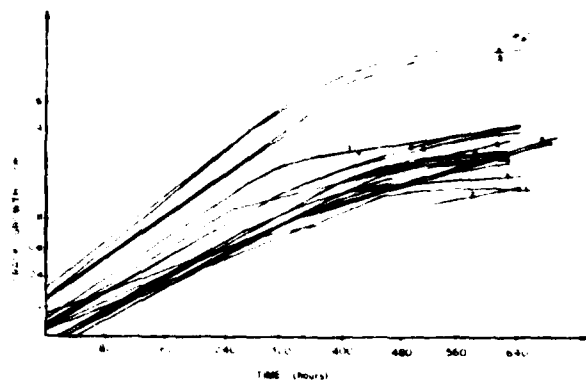


FIGURE 2 — Rate of stress corrosion crack growth (plateau velocities) in 9 DCB specimens as a function of time; AA 7075-T651 in 1 N NaClO₂.

TABLE 1 — Stress Corrosion Crack Growth Rates (Plateau Velocities) for AA 7075-T651 in 1 N NaClO₂.

Specimen Number	61	65	70
Slope (10 ⁶ cm/sec)	0.53	0.64	0.65
Intercept	+0.04	+0.07	+0.04
Specimen Number	31	35	40
Slope (10 ⁶ cm/sec)	0.61	0.77	0.80
Intercept	+0.05	+0.09	+0.08
Specimen Number	1	5	10
Slope (10 ⁶ cm/sec)	0.96	0.96	0.72
Intercept	+0.12	+0.12	0.00

Results and Discussion

Statistical Rate of Stress Corrosion Crack Growth

A plot of stress corrosion crack growth in 1 N NaClO₂ solution as a function of time for nine specimens is given in Figure 2. The plot commences with the mechanical overload value of K, the stress intensity, the so-called "pop-in" value. These curves consist approximately of two straight lines, the slope of the first straight line being the plateau slope in the stress intensity-log crack growth plot. The slopes and intercepts of the initial straight lines for the nine samples are recorded in Table 1, which should be keyed to Figure 1 to locate an individual specimen in the plate. For each specimen two values are given because the measurement of crack growth differs for each side of the specimen. The arithmetic mean of the slopes is 0.809×10^{-6} cm sec⁻¹ with a standard deviation of $\sigma = 0.173 \times 10^{-6}$. This yields a reliability, M, of $0.81 \pm 0.07 \times 10^{-6}$ cm sec⁻¹ or 8.6% at the 90% confidence level. The reliability was calculated from the relationship:

$$M = (\text{calculated mean}) \pm t \frac{\sigma}{n} \quad (1)$$

where t has a value of 1.740 for 17 degrees of freedom and n is the number of specimens. With this precision it would be concluded that the rate of stress corrosion crack growth rate as indicated by the slope is slightly greater for the specimens taken from the edge of the plate than the center.

The scatter of the data obtained with these nine samples, along with the crack growth data obtained from other specimens run in 1 N NaClO₂ and taken from the same plate (E) is readily seen with a histogram of the type drawn in Figure 3. For comparison, twelve measurements of crack growth in the

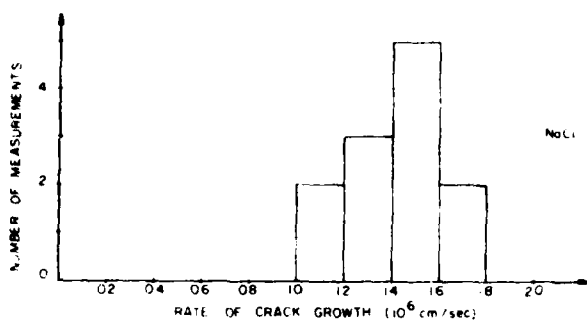
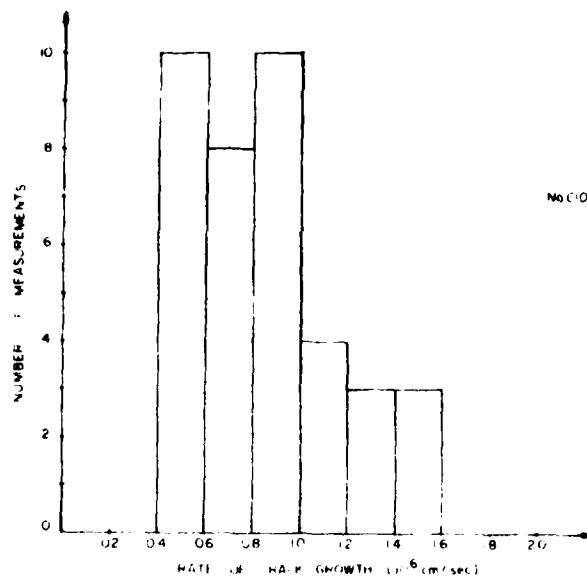


FIGURE 3 — Histogram showing distribution of stress corrosion crack growth rates (plateau velocities) in DCB specimens in AA 7075-T651: Top—in 1 N NaClO₄ solution; Bottom—in 1 N NaCl solution.

same plate of AA 7075-T651 in 1 N NaCl are drawn with the same abscissa. The mean value of the slope of the NaCl curve is 1.43×10^{-6} cm sec⁻¹ with a standard deviation of $\sigma = 0.185 \times 10^{-6}$ cm sec⁻¹. This gives a reliability of $M = 1.43 \pm 0.096 \times 10^{-6}$ cm sec⁻¹ or 6.7%.

From fracture mechanics theory and the dimensions of the sample as the crack is advancing, it is possible to calculate the stress intensity factor, K, which defines the stress field at the leading edge of the crack.⁴ A plot of K versus the logarithm of the growth rate given in Figure 4 for cracking in 1 N NaClO₂ is compared with a similar plot for 1 N NaCl. The considerable scatter of the data is obvious. Further, from this plot it is possible to calculate the value of the threshold stress intensity. The extrapolated value, usually labeled K_{ISSC}, is between 9.1 to 12.5 MN/m^{3/2} or 8.27 to 11.36 ksi√in. The value at the shoulder is 12.5 to 15 MN/m^{3/2} or 11.36 to 13.64 ksi√in. From the plot of the data collected with 1 N NaCl an extrapolated value of 7.8 MN/m^{3/2} or 7.02 ksi√in is obtained. This compares with a value of 5 ksi√in reported¹ for AA 7075-T651 run in 3.5% NaCl solution (obviously a different plate). The indication is that the K_{ISSC} is appreciably higher in NaClO₂ solution than in NaCl solution.

Concentration Effect

A series of experiments was run to establish the concentration effect of NaClO₂. Based on four measurements at perchlorate concentrations of from 0.01 N to 2.5 N, there is no systematic change of crack growth rate with concentration (Table 2). The absence of a concentration effect suggests

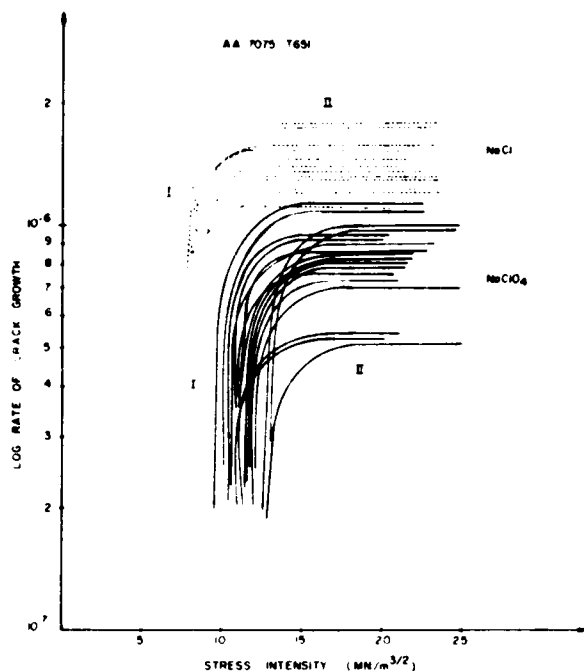


FIGURE 4 — Relationship between, K, the stress intensity and the logarithm of the rate of stress corrosion crack growth: Upper, dotted line, in 1 N NaCl; lower, solid line, in 1 N NaClO₄.

TABLE 2 — Stress Corrosion Crack Growth Rates (Plateau Velocities) for AA 7075-T651 as a Function of NaClO₄ Concentration

Concentration of NaClO ₄	Rate of Crack Growth (x10 ⁶ cm/sec)	Mean (x10 ⁶ cm/sec)	Standard Deviation (x10 ⁶ cm/sec)
0.01 N	0.82, 0.78, 1.25, 1.53	1.10	0.36
0.1 N	0.66, 1.19, 0.76, 0.99	0.90	0.24
0.5 N	1.23, 0.92, 0.90, 0.85	0.98	0.17
1.0 N	0.88, 0.82, 0.53, 0.57	0.70	0.18
2.0 N	0.58, 0.45, 1.30, 1.40	0.93	0.49

that there is no specific interaction between the perchlorate ion and aluminum.

Local Chemistry

Analyses of the solution within the stress corrosion crack must be conducted at two stages to give a complete description of the local chemistry. The active crack growth is occurring in phase II of the stress intensity-log crack growth plot (compare Figure 4). In phase I it is reasonable that diffusion effects should be altering the composition.

The pH of the bulk 1 N NaClO₄ solution was 6.5. The pH at the crack tip, when the crack growth was in phase II, or, in the active crack tip, varied in the range of 6.3 to 6.9. Over a period of time, as the rate of crack growth decreased or as the specimen went from phase II to phase I in Figure 4, the pH rose slowly to 7.2. This behavior is contrasted with that occurring in 1 N NaCl solution. The measurement of the pH in the stress cracks of specimens used to construct the histogram for the NaCl solution in Figure 3 gave values of 3.0 to 3.2 in phase II and 4.4 to 4.6 in phase I. These latter measurements follow what has been observed before for NaCl and Na₂SO₄ solutions.⁹

The concentration of aluminum ion measured by the quinalizarin method described above gave for the nine samples concentrations of 0.01, 0.005, 0.01, 0.01, 0.01, 0.005, 0.005, 0.01, 0.01 molar, or, all analyses fell in the range of 0.005

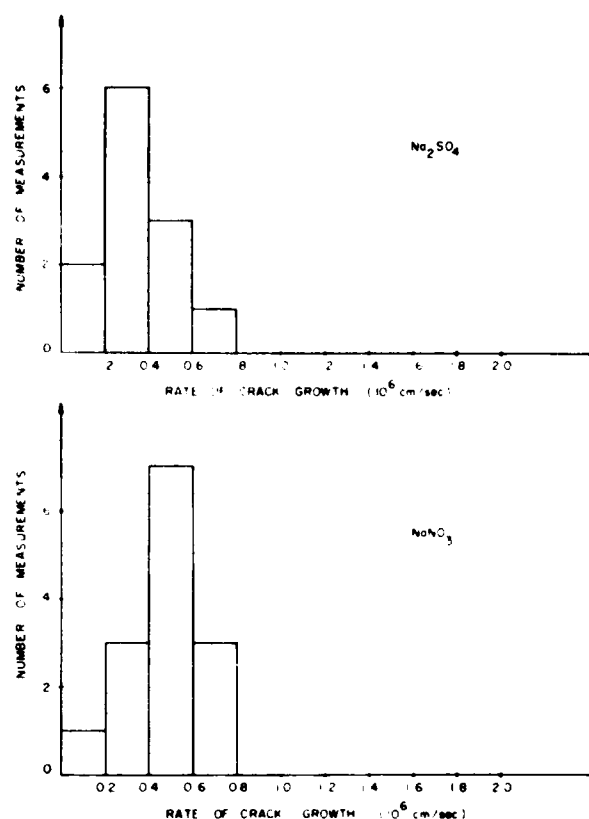


FIGURE 5 — Histogram showing distribution of stress corrosion crack growth rates (plateau velocities) in DCB specimens in AA 7075-T651: Top—in 1 N Na₂SO₄ solution; Bottom—in 1 N NaNO₃ solution.

to 0.01 M. Away from the advancing crack and in the precrack and corrosion area, the aluminum ion concentration reached 0.5 M.

Comparison of Perchlorate with Other Anions

The comparison of the stress corrosion cracking behavior of AA 7075-T651 in perchlorate solutions and chloride solutions has been shown graphically in Figure 3. Some data on nitrate and sulfate have been reported previously⁹ and new data for crack growth rates in 1 N Na₂SO₄ and 1 N NaNO₃ are shown in Figure 5. Note that the horizontal scale (rate of crack growth) is the same as that in Figure 3 which allows direct comparison for the four solutions. In 1 N NaNO₃ solution, the mean rate for 14 measurements was 0.48×10^{-6} cm/sec with a σ of 0.13×10^{-6} cm/sec and a reliability, M, of $0.48 \pm 0.064 \times 10^{-6}$ cm/sec, or 13%. In 1 N Na₂SO₄ solution the mean of 11 measurements was 0.29×10^{-6} cm/sec with a σ of 0.13×10^{-6} cm/sec. The reliability, M, was $0.29 \pm 0.07 \times 10^{-6}$ cm/sec, or 24%. The low precision of the measurements in sodium sulfate solution is due in part to the low rate of crack growth which means that the recorded measurement is the difference between two small numbers read on the millimeter scale. The rates in nitrate and sulfate solutions are obviously quite low. For comparison, the mean crack growth rate of this particular plate of AA 7075-T651 in distilled water is 0.47×10^{-6} cm/sec.

Another qualitative comparison of the susceptibility for crack propagation in these different electrolytes is the time required for the crack to continue to grow in the precracked specimen after immersion in the electrolyte. This is admittedly

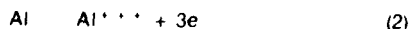
a subjective observation. In NaCl solution, crack growth resumes after 6 hours; in NaClO₄ solution, 12 hours; in Na₂SO₄ solution about 6 days; and in NaNO₃ solution about 6 days

Conclusions

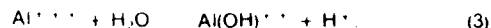
In terms of chemical reactivity, perchlorate can be classified as an indifferent or noncomplexing anion. The cracking rate in 1 N NaClO₄ for the specific plate used in this study was 0.81×10^{-6} cm/sec with a reliability at the 90% level of 8.6%. For comparison, a solution containing a reactive anion (1 N NaCl) gave a crack growth rate of 1.43×10^{-6} cm/sec with a reliability of 6.7% or a factor of 1.77 increase in rate. Sulfate is also a reactive anion, but because of the nature of the reaction product which is formed, is passivating. There is good evidence¹⁰ that sulfate forms a low energy aluminum hydroxy sulfate compound that passivates the aluminum surface toward further corrosion. The cracking rate in sulfate is very low. The nitrate ion is usually passivating and stress corrosion crack growth is usually also slow in 1 N NaNO₃ solution. However, previous experimentation¹¹ has demonstrated that under certain circumstances crack growth can be rapid. These conditions include cathodic polarization or circumstances by which an aluminum surface free of oxide is in some way developed. Under these special conditions, nitrate ion is reduced to ammonia and cracking is accelerated. Therefore, in a practical sense, the effect of the nitrate ion on stress crack growth would have to be characterized as *unpredictable*. Considering the precision and reliability of these tests, it must be concluded that to develop significant relationships between such factors as crack growth rate and electrolyte composition, a large number of specimens must be tested. Insofar as the DCB test is concerned, the reliability of a single test will not be better than 5 to 10%. This means that in evaluating various parameters in the stress corrosion process or in attempting to develop a basic mechanism, if altering various factors do not yield changes in rate greater than about 10%, that factor cannot be judged significant.

The relatively high pH of 6.3 to 6.9 measured in the active crack in NaClO₄ solution is at variance with measured values in NaCl and Na₂SO₄ solution.⁹ For NaCl solutions, many investigators have reported values in the range of 3.2 to 3.4 which have been explained on the basis of Al³⁺ hydrolysis. The high pH appears to go with a low aluminum ion concentration (0.005 to 0.01 M). However, crack growth is appreciable in sodium perchlorate solution, which means that the conventional correlation between crack growth rate and low pH does not hold for this specific electrolyte.

These results again emphasize that it is the local solution composition that is important. When an oxide-free aluminum surface, such as the crack tip in a stress corroding specimen, is exposed to an aqueous solution, the instantaneous reaction is



followed by the very fast reaction



The hydroxy aluminum complex will go directly to Al(OH)₃ in the absence of complexing species. Thus, the alloy under tensile stress in distilled water will crack, admittedly at a low rate, and the solution in the crack will contain soluble aluminum species such as Al(OH)²⁺ and Al(OH)₂⁺.

All of these tests suggest that if the objective of a particular investigation is to evaluate nonchemical effects, e.g., metallurgical parameters such as heat treatment or alloy composition, it would be sensible to conduct the test in NaClO₄ solution rather than NaCl solution. This would eliminate specific interactions such as those that occur with chloride, e.g., the formation of transitory species that enhance metal dissolution.

Acknowledgments

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